GaN and AlGaN Halide Vapor Phase Epitaxy

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Research Goals and Progress

- Develop HVPE Growth of AlGaN
- Investigate ‘Lift-off’ Technologies for GaN
  - ELO on fine line features
  - Alternative Buffer and substrates

Approach:

1. Impact of nucleation on film properties
2. Analysis of AlGaN and GaN HVPE systems for high throughput and uniform growth
3. Design through combined computational Fluid dynamics and chemistry inputs
3. Growth of materials for other devices efforts

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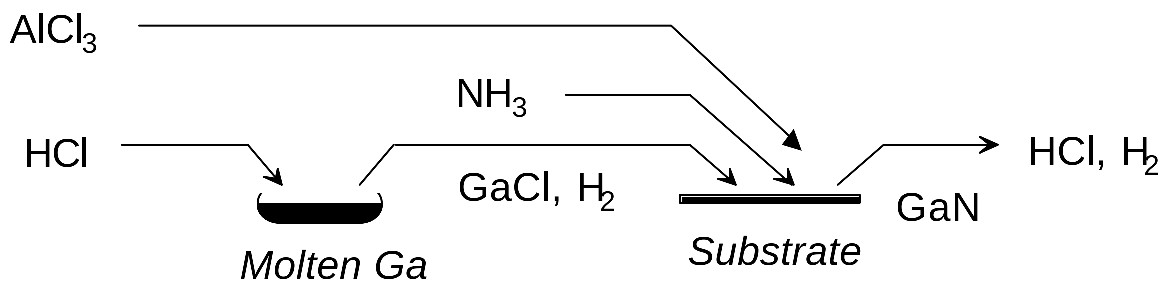
HVPE GaN (AlGaN) Growth Chemistry



$HCl + Ga \rightarrow GaCl + \frac{1}{2} H_2$
(850°C, 90% Efficient)

$$GaCl + NH_3 \rightarrow GaN_{(s)} + HCl + H_2$$

$$AlCl_3 + NH_3 \rightarrow AlN_{(s)} + 3HCl$$

- **NH_3:HCl Ratio is Typically 30:1**
- **Growth Rates Typically 0.3 μm/min.**

Low Cost, High Growth Rate, and Possibility of Expanding to Multi-Wafer Processing.

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AlN-GaN Solid Solution

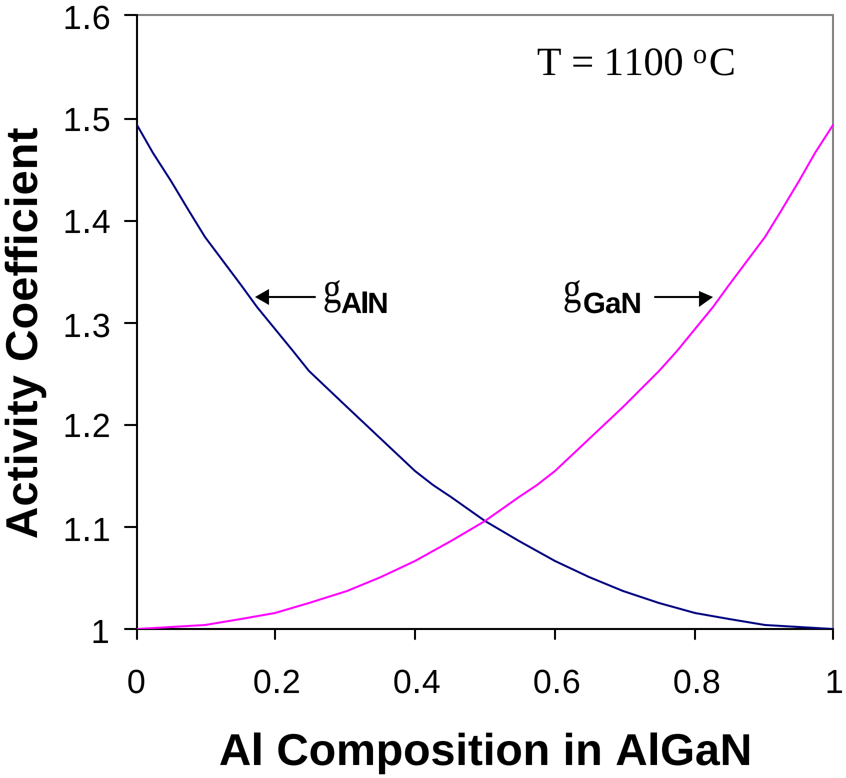
- Small deviation from ideal solution behavior

  using DLP model

  $\Omega_{AlN\text{-}GaN} = 4580$ J/mol

  $1 \leq \gamma_{AlN}, \gamma_{GaN} < 1.5$

- AlN is miscible in GaN over all composition range



Thermodynamic of $AlCl_3$ formation

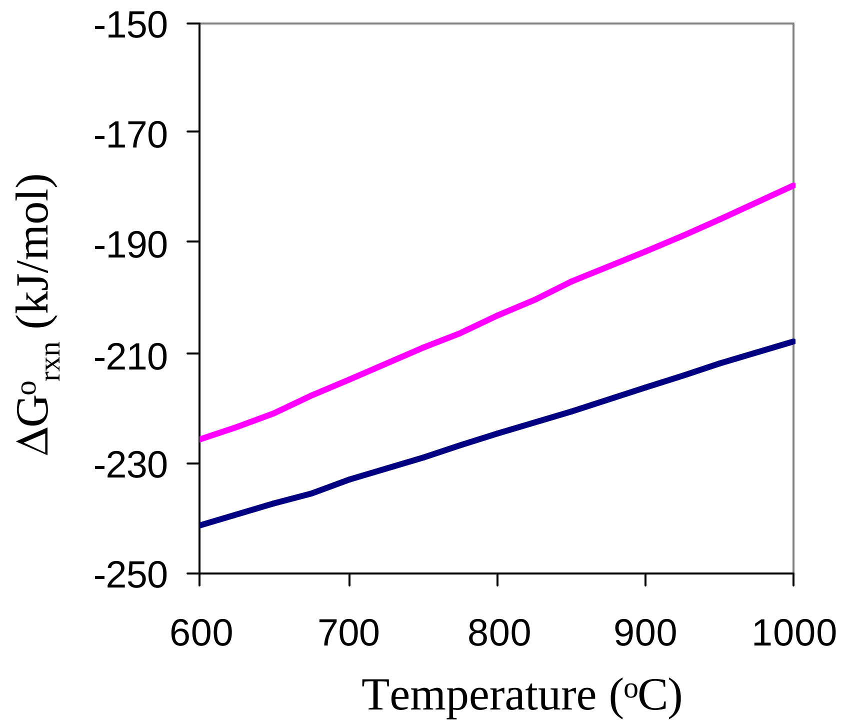
Reaction inside Al boat :

$$Al_{(s)} + 3\ HCl \longrightarrow AlCl_3 + 3/2\ H_2$$

However using N_2 carrier, there is a competing reaction:

$$Al_{(s)} + 1/2\ N_2 \longrightarrow AlN$$

Therefore, N_2 cannot be used as carrier gas for $AlCl_3$ formation



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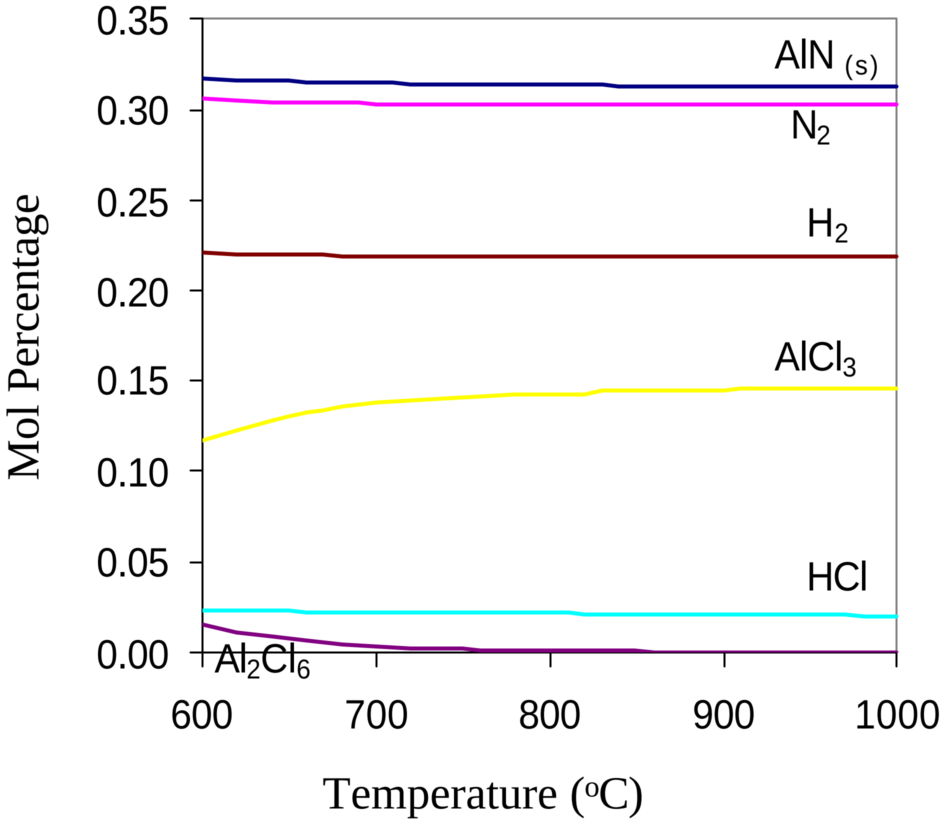
$AlCl_3$ Equilibrium

Equilibrium for 33% Al(s), 33% N_2, and 33% HCl Mixture



When both N_2 and HCl present with Al metal, AlN formation is more favorable than $AlCl_3$

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Homogeneous Reactions

- AlN reaction is more favored than GaN reaction
- When $AlCl_3$ mixes with NH_3 in the gas phase, they reacts instantaneously producing:
  - AlN powder
  - three moles of HCl that will affect film growth

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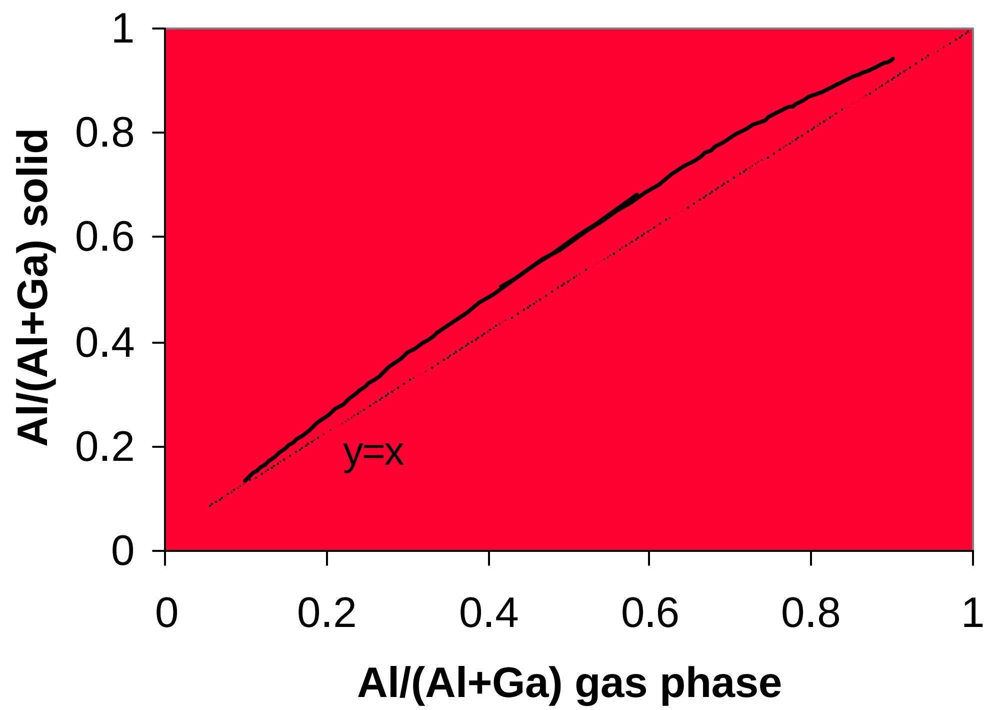
Al Concentration in AlGaN

$$\left[\frac{\mathrm{Al}}{\mathrm{Al}+\mathrm{Ga}}\right]_{\mathrm{solid}} > \left[\frac{\mathrm{Al}}{\mathrm{Al}+\mathrm{Ga}}\right]_{\mathrm{gas\ phase}}$$

– AlN is more stable than GaN

– H_2 shifts the GaN reaction to the left

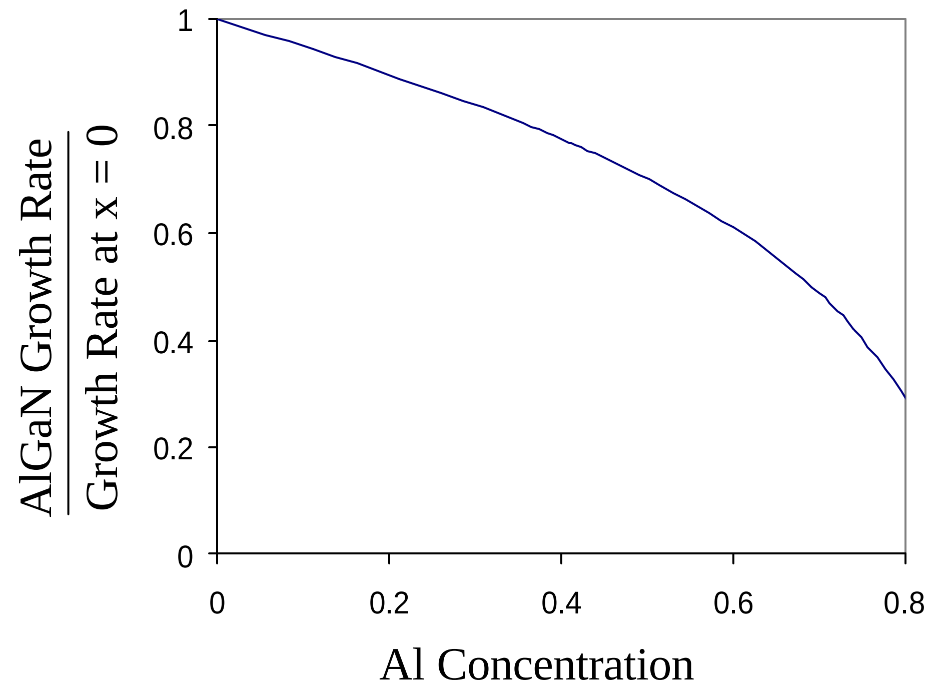


Effect of AlN Reaction on Overall Growth Rate

AlGaN growth rate decreases with AlN concentration

– one mole of AlN produces three moles of HCl

– driving force for GaN etching increases as P_{HCl} increases



$$\Delta G_{\text{GaN etching}} = \Delta G^o_{rxn} + RT \ln\left(\frac{P_{GaCl}\, P_{H_2}^{\;1/2}\, P_{N_2}^{\;1/2}}{P_{HCl}}\right)$$

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Competing Reactions at the Growth Surface

- GaN
  - Growth

$GaCl + NH_3 \leftrightarrow GaN_{(s)} + HCl + H_2$

  - Etching

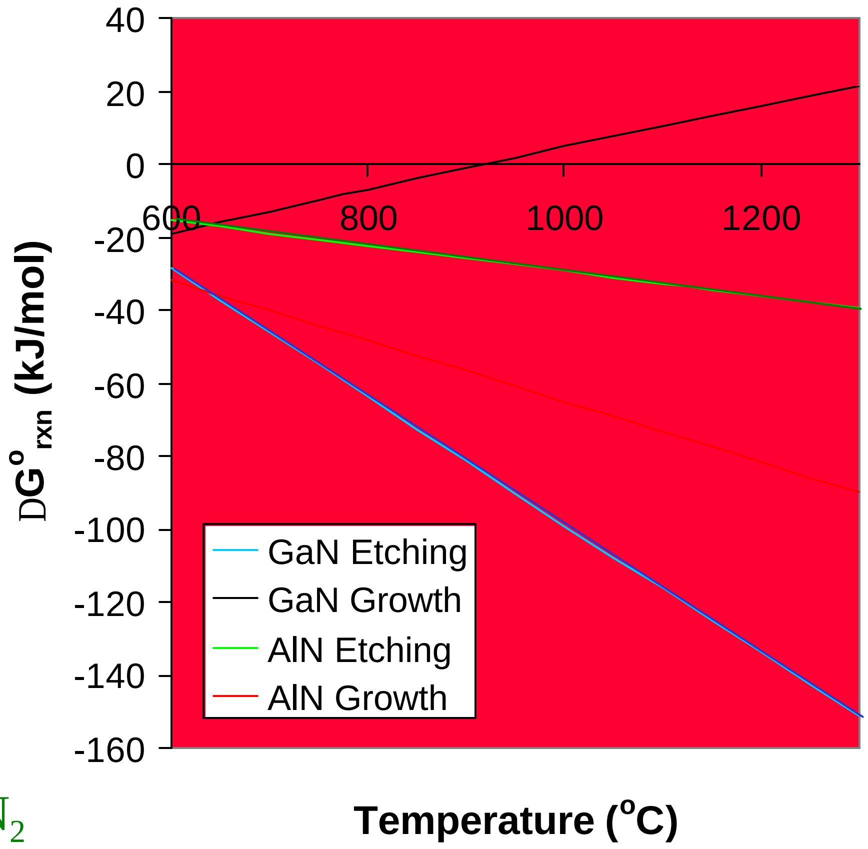
$GaN_{(s)} + HCl \leftrightarrow GaCl + 1/2\ H_2 + 1/2\ N_2$

- AlN
  - Growth

$AlCl_3 + NH_3 \leftrightarrow AlN_{(s)} + 3\ HCl$

  - Etching

$AlN_{(s)} + 3\ HCl \leftrightarrow AlCl_3 + 3/2\ H_2 + 1/2\ N_2$



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Temperature effect on $Al_xGa_{1-x}N$ Growth

- AlN growth is favorable at higher temperature than GaN

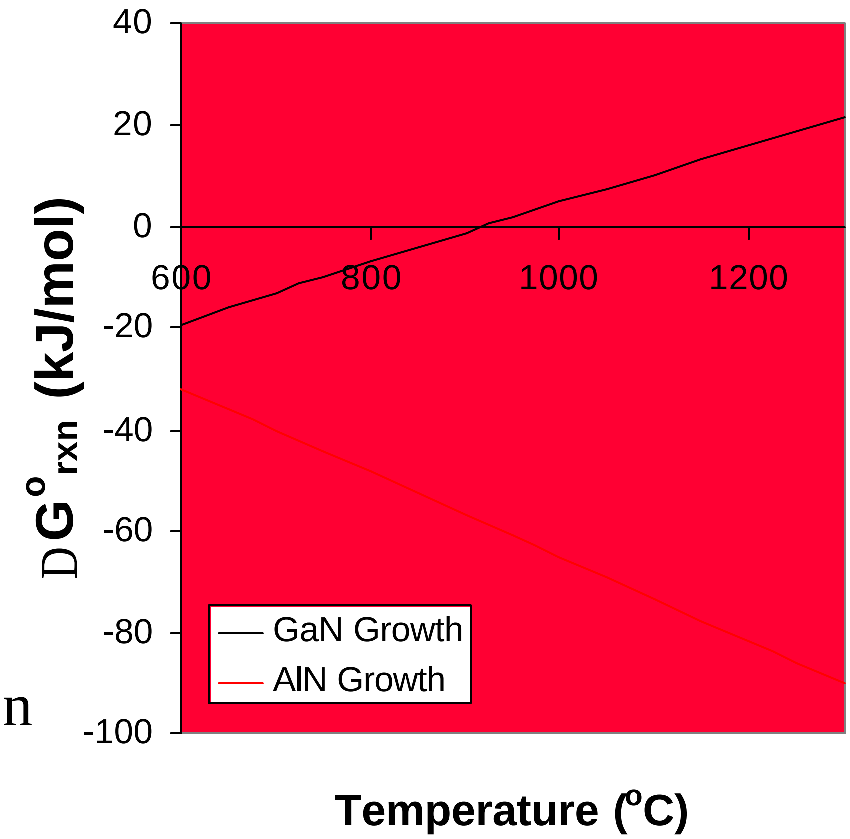
$GaCl + NH_3 \longleftrightarrow GaN_{(s)} + HCl + H_2$

$\Delta H_{rxn,\,1050\,^oC} = -67.37$ kJ/mol (Exothermic)

$AlCl_3 + NH_3 \longleftrightarrow AlN_{(s)} + 3\,HCl$

$\Delta H_{rxn,\,1050\,^oC} = 41.76$ kJ/mol (Endothermic)

- Growth temperature is proportional with Al concentration



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Impurities

- $AlCl_3$ reacts with quartz to form $Al_2SiO_{5(s)}$ and $Al_2O_{3(s)}$
  - Use reactor liner from Al_2O_3
  - Al boat and gas lines from Al_2O_3

- Traces of O_2 and H_2O react with GaCl and $AlCl_3$ to form $Ga_2O_{(s)}$, $Ga_2O_{3(s)}$, and $Al_2O_{3(s)}$

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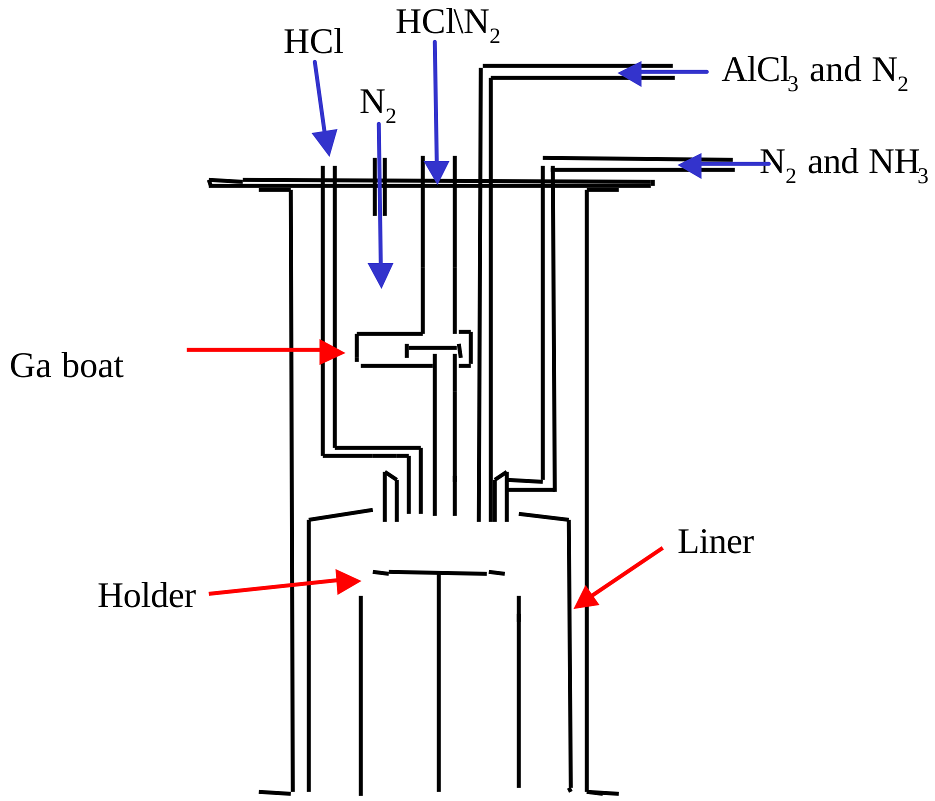
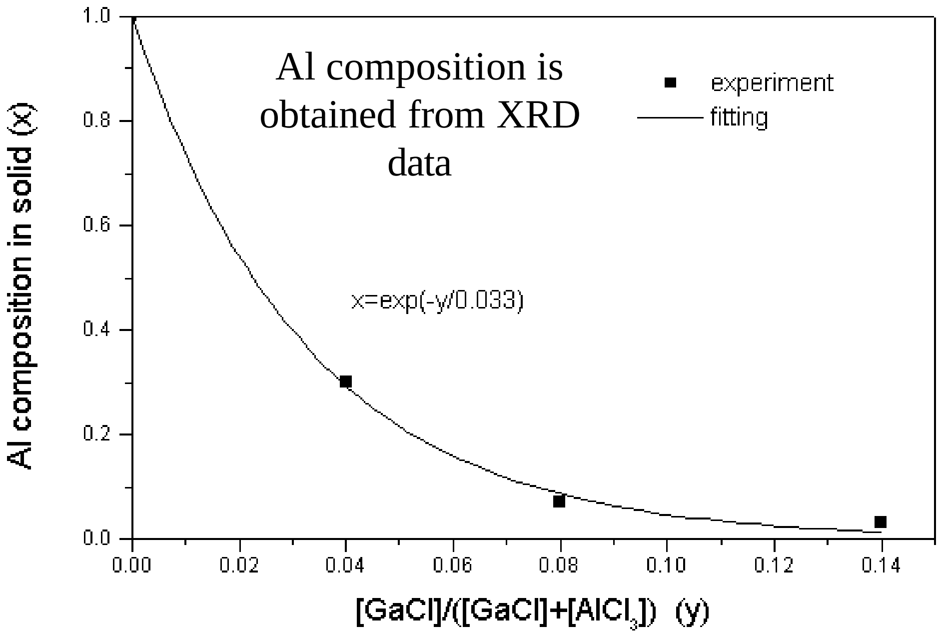
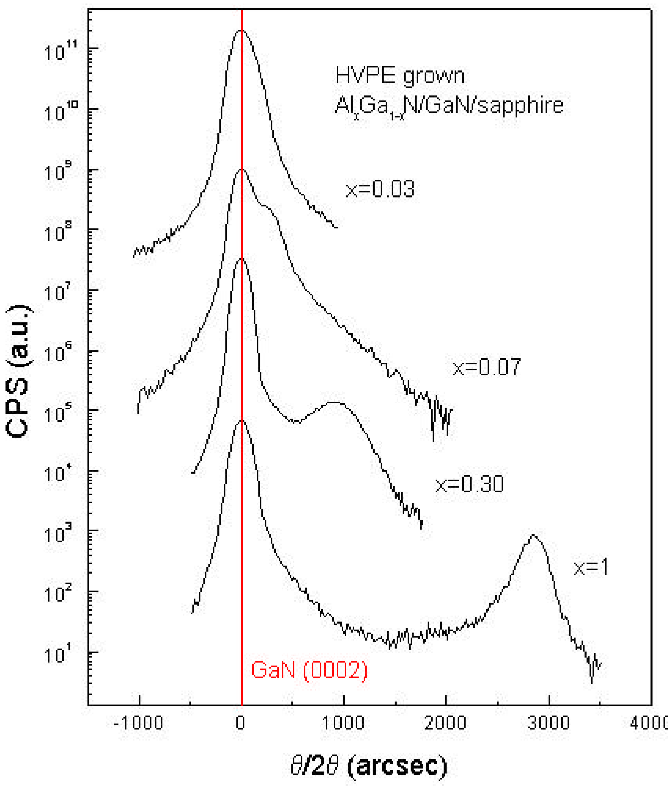
Initial AlGaN System: Use of $AlCl_3$ Solid Sources



Al incorporation during growth

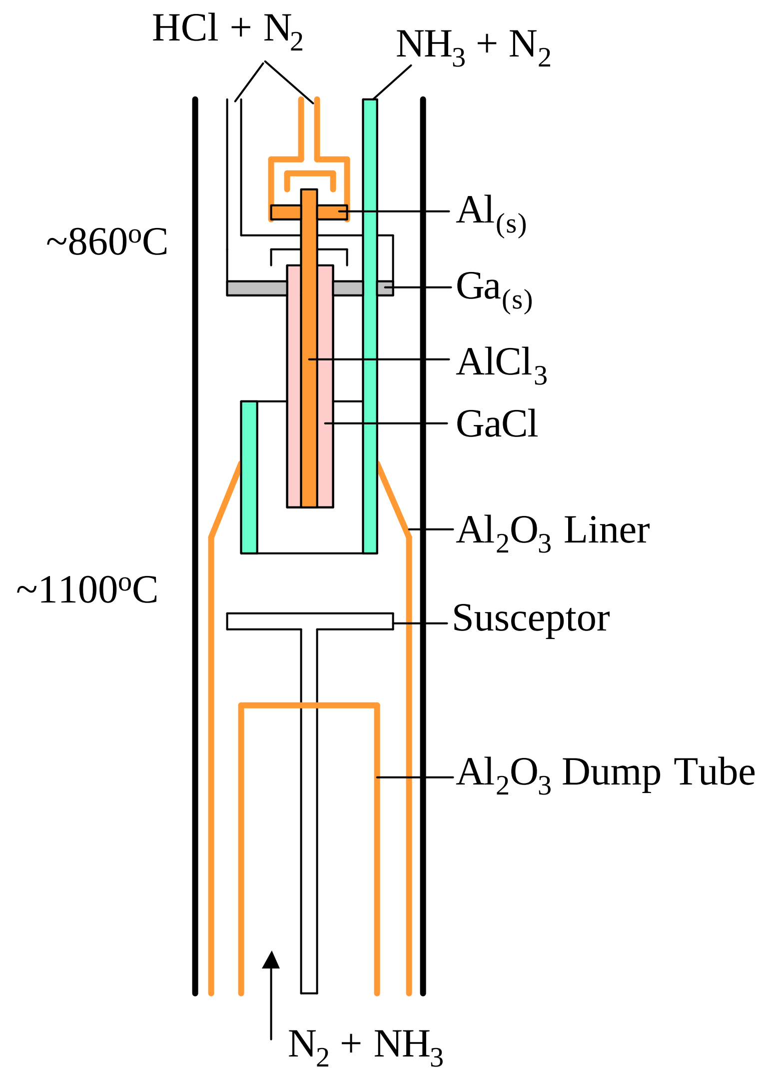




- Al composition in solid is coupled to the Ga source mole fraction in gas phase
- Low incorporation rate of Al may be due to high reactivity between $AlCl_3$ and NH_3 in gas phase

$Al_xGa_{1-x}N$ Growth System

- Vertical reactor
- P = 1 atm
- Group III precursors are Al and Ga metal
- Alumina parts at critical points
- Growth temperature can be adjusted up to 1500 °C



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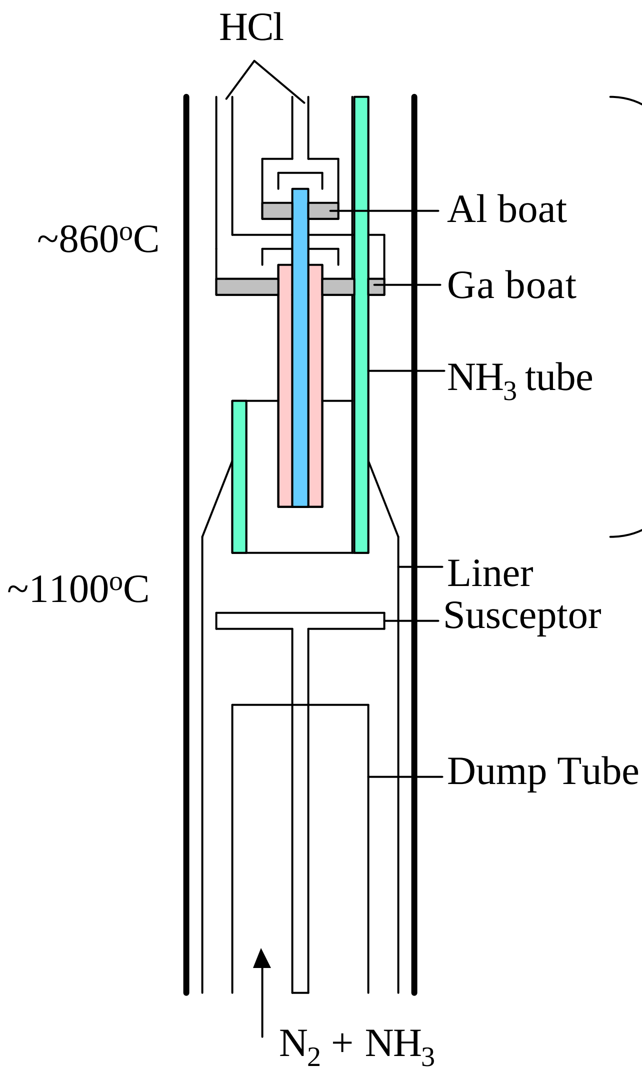
HVPE Reactor Design



Geometry of the gas delivery system inside the cylindrical reactor is very critical on the film growth:

- crystallinity of film
- uniformity
- occurrence of gas phase reaction

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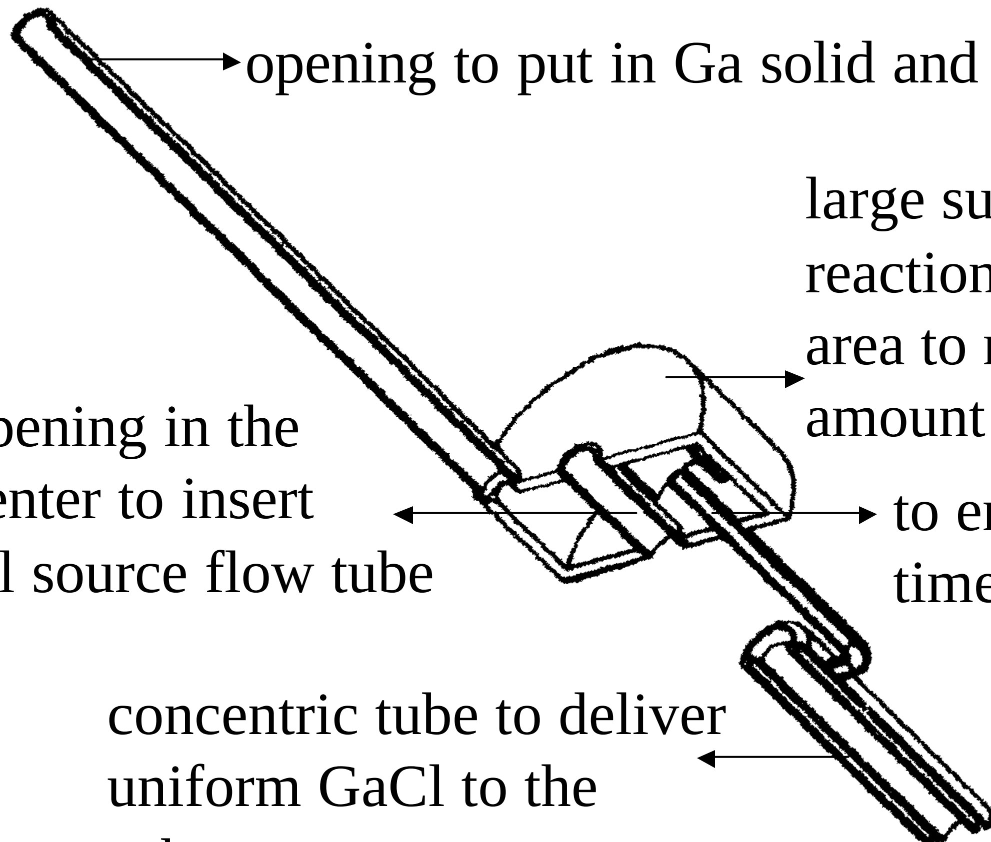
Ga Boat Design

$$Ga_{(s)} + HCl \longrightarrow GaCl + 1/2\ H_2$$



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GaCl Flow Streaming Problem

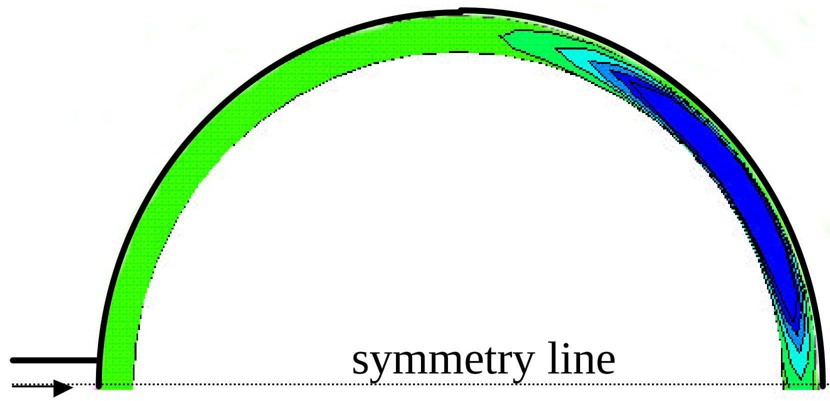
GaCl flow streaming causes:

- severe growth non-uniformity (~1000% across the substrate)
- poor nucleation

non-uniform gas entry

flow only coming out from this side

Flow Simulation



Bottom Viem

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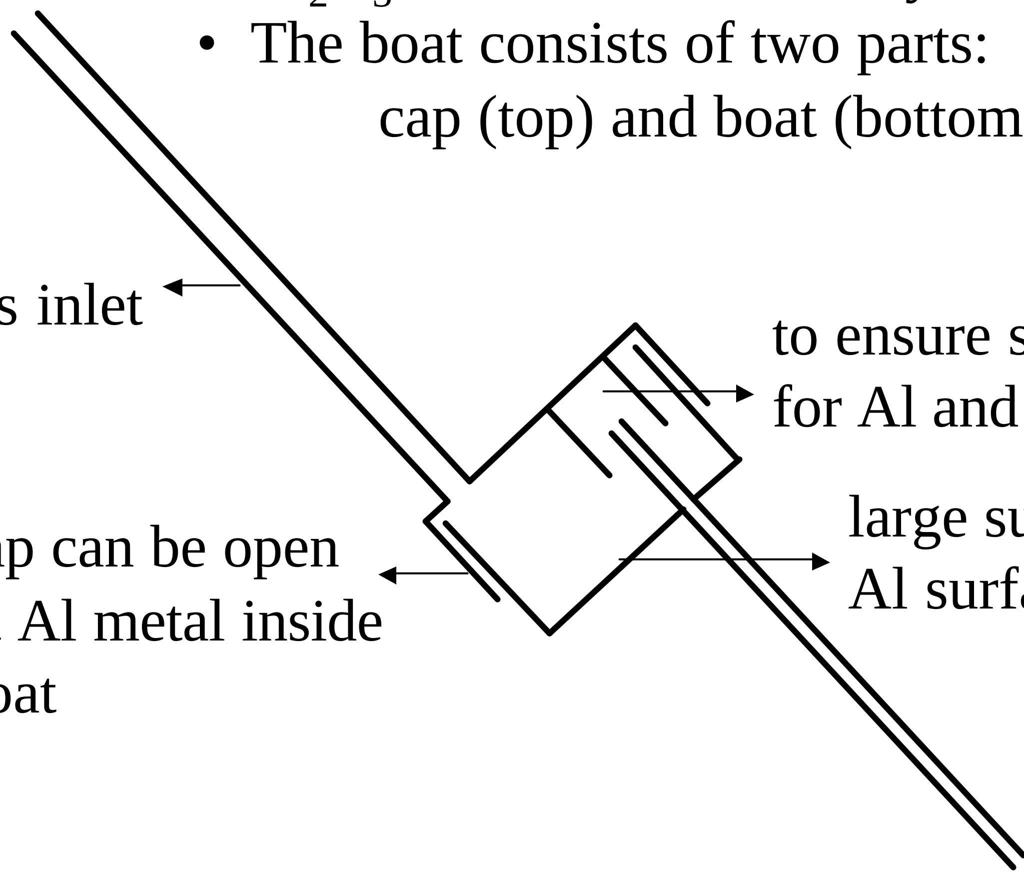
Al Boat Design

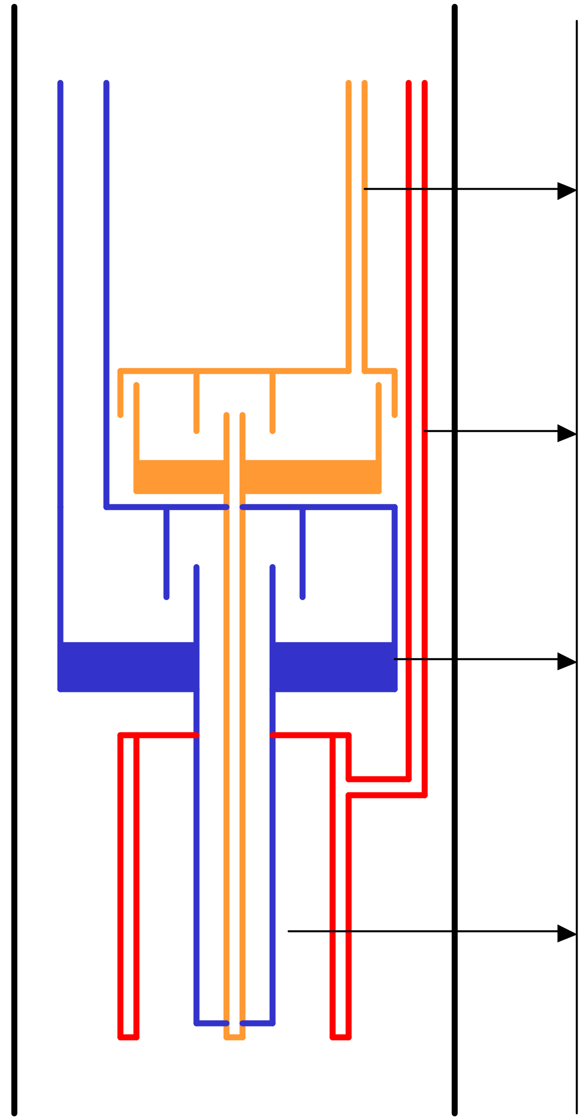
$$Al_{(s)} + 3\,HCl \longrightarrow AlCl_3 + 3/2\,H_2$$

- Al_2O_3 ceramic material only has limited shape
- The boat consists of two parts:

  cap (top) and boat (bottom)



Overall Gas Delivery System



Alumina Al boat with liquid Al inside, supported by Ga boat

NH_3 tube to separate NH_3 and GaCl and $AlCl_3$ to prevent gas phase reaction

Ga boat with liquid Ga inside

Annular tubes for uniform growth

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Computational Modeling

- To find optimum GaCl, NH_3, and N_2 velocity:
  - reduce gas phase reactions (N_2 is used as barrier to prevent GaCl and NH_3 mixing in the gas phase)
  - increase film uniformity

- Governing Equations:
  - Mass $\Delta \bullet (\rho \upsilon) = 0$
  - Momentum $\rho \upsilon \bullet \Delta \upsilon = - \Delta P + \Delta \bullet [\mu \Delta \upsilon + (\Delta \upsilon)^T - (2/3) \mu I \Delta \bullet \upsilon]$
  - Species Continuity $\Delta \bullet (c x_i \upsilon) = \Delta \bullet (c D_i (\Delta x_i))$

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Computational Domain

Assumptions:

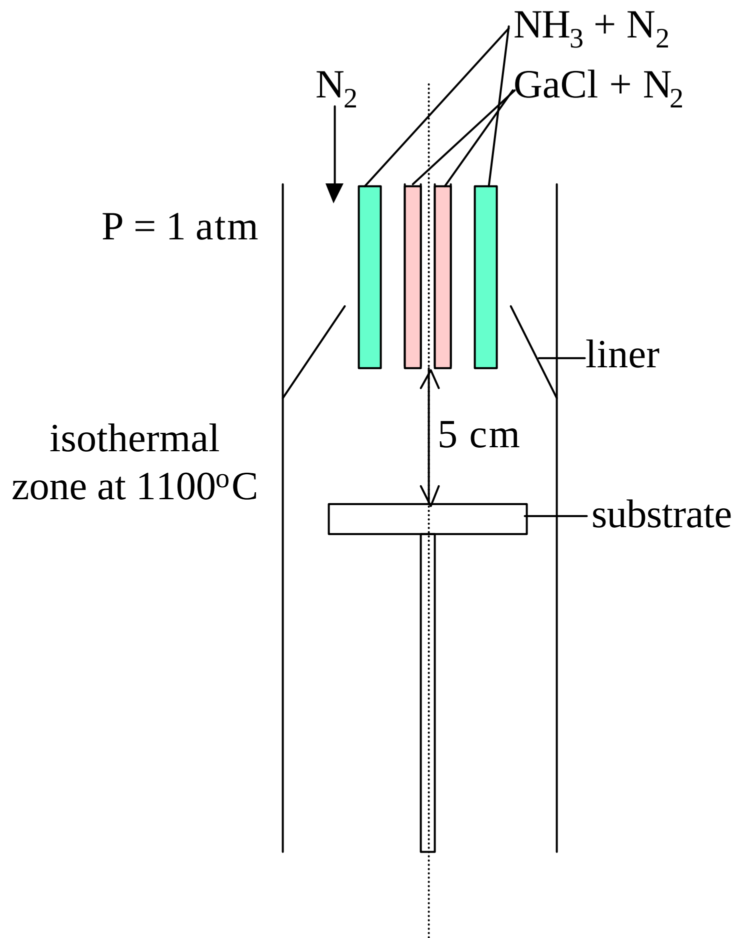
– 2-dimension model of GaN growth

– instantaneous gas phase reaction between NH_3 and GaCl, resulting in $GaN_{(s)}$ deposition at GaCl and NH_3 tubes

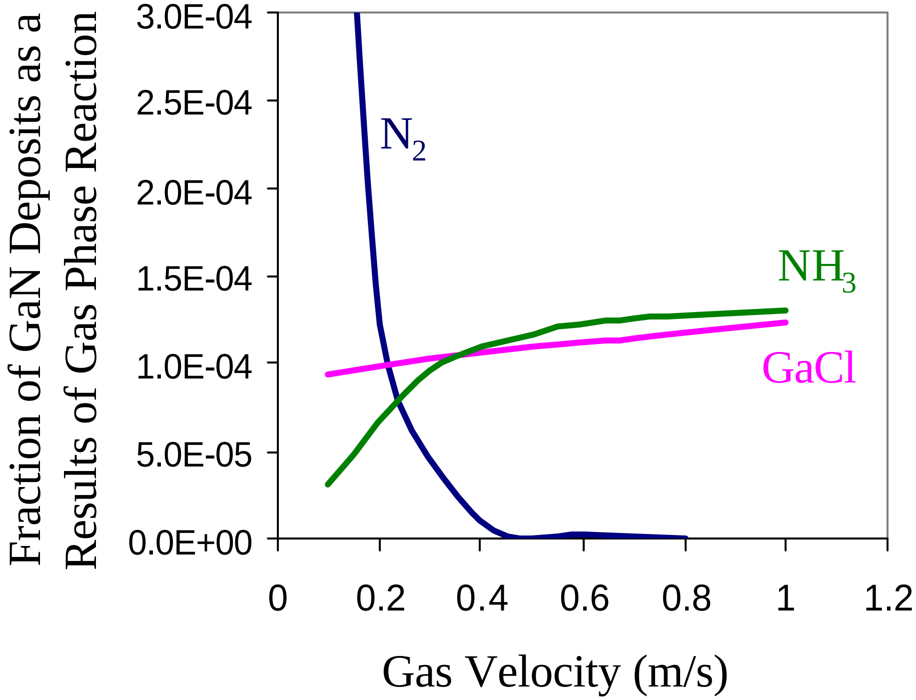
– second temperature zone (growth zone)

– fully developed flow

– V/III = 60



Velocity vs. Gas Phase Reaction



- As barrier between GaCl and NH_3, N_2 velocity higher than 0.2 m/s is required to minimize gas phase reaction
- Increase GaCl velocity only has a small effect on gas phase reaction
- NH_3 velocity has linear effect at the beginning and negligible effect at high values

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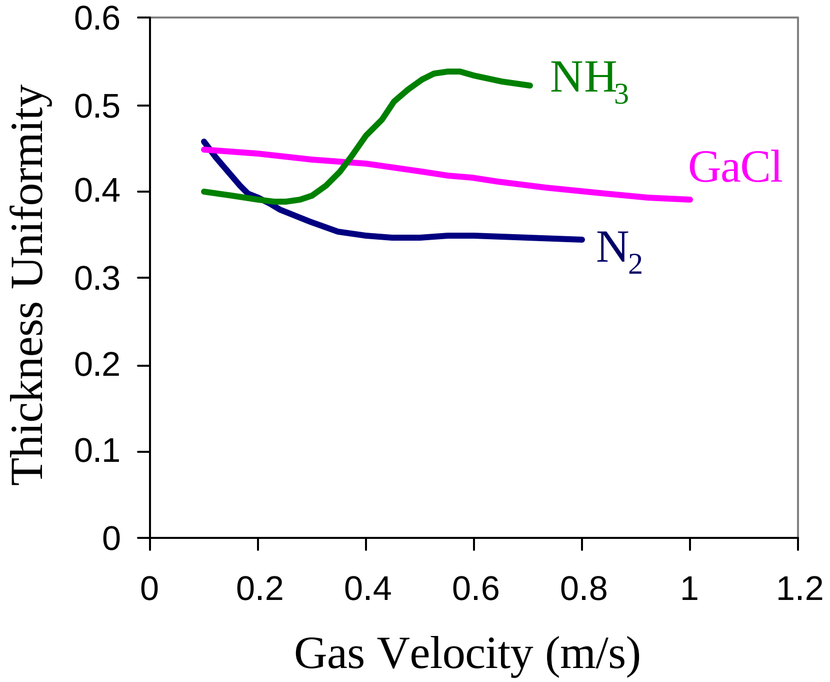
Velocity vs. Film Uniformity



- Uniformity is improved as GaCl and N_2 velocities decrease

- Increase NH_3 velocity improves film uniformity

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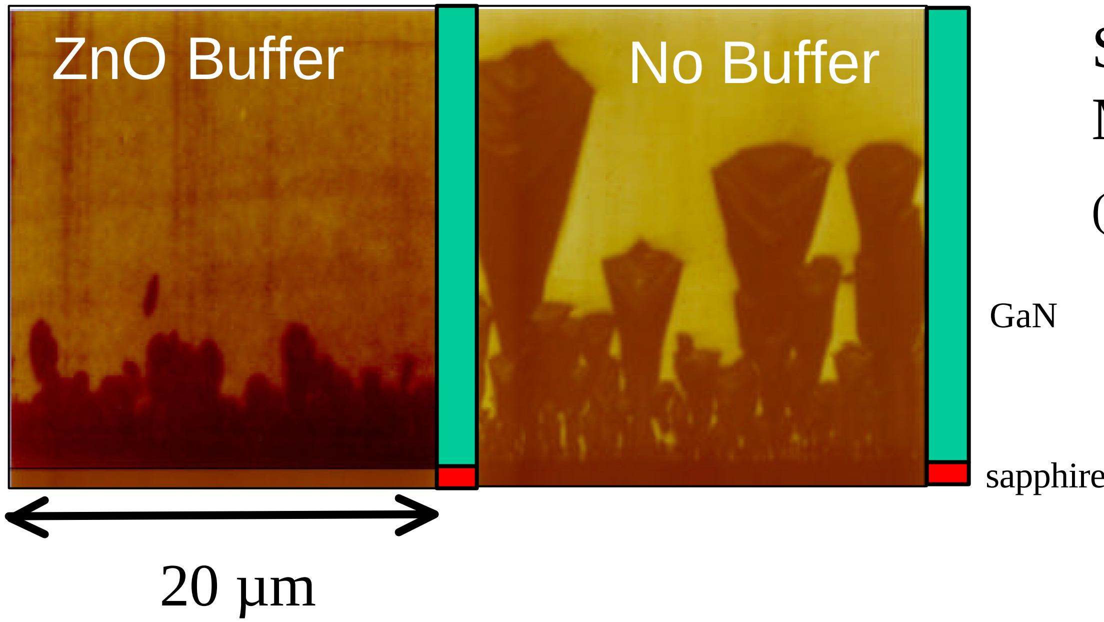
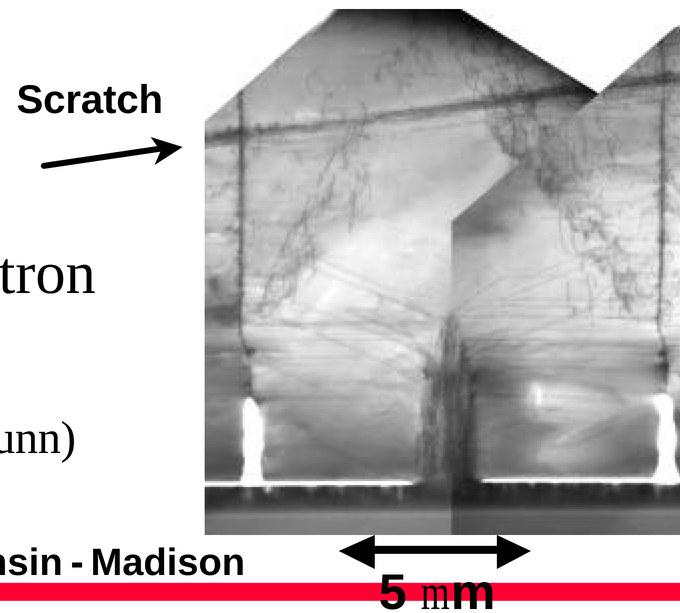


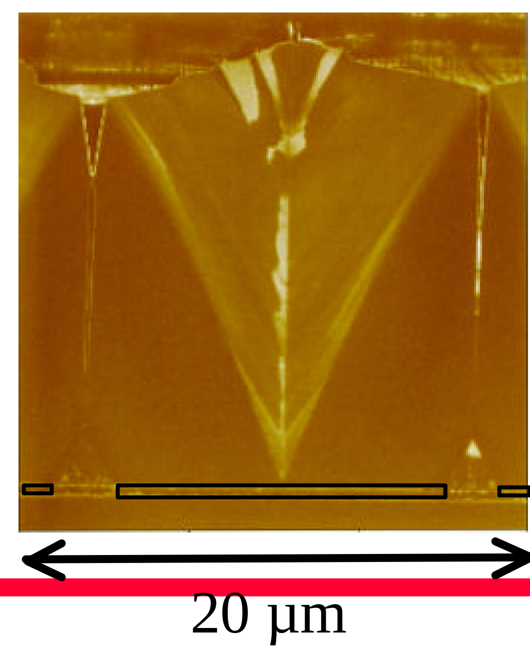
Scanning Capacitance Measurements

(Julia Hsu, Lucent – Bell Labs.)

Transmission Electron Microscopy

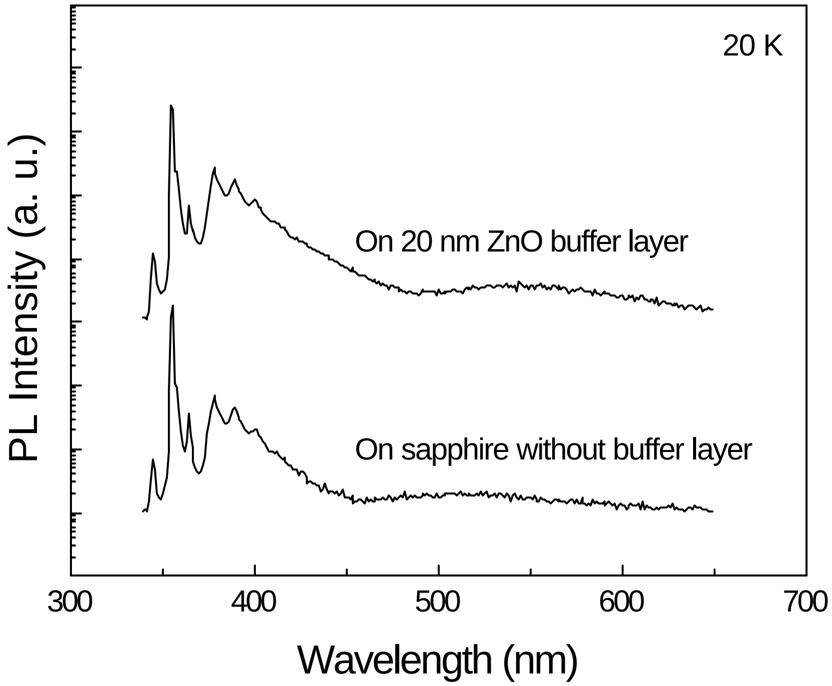
(S.E. Babcock and K. Dunn)





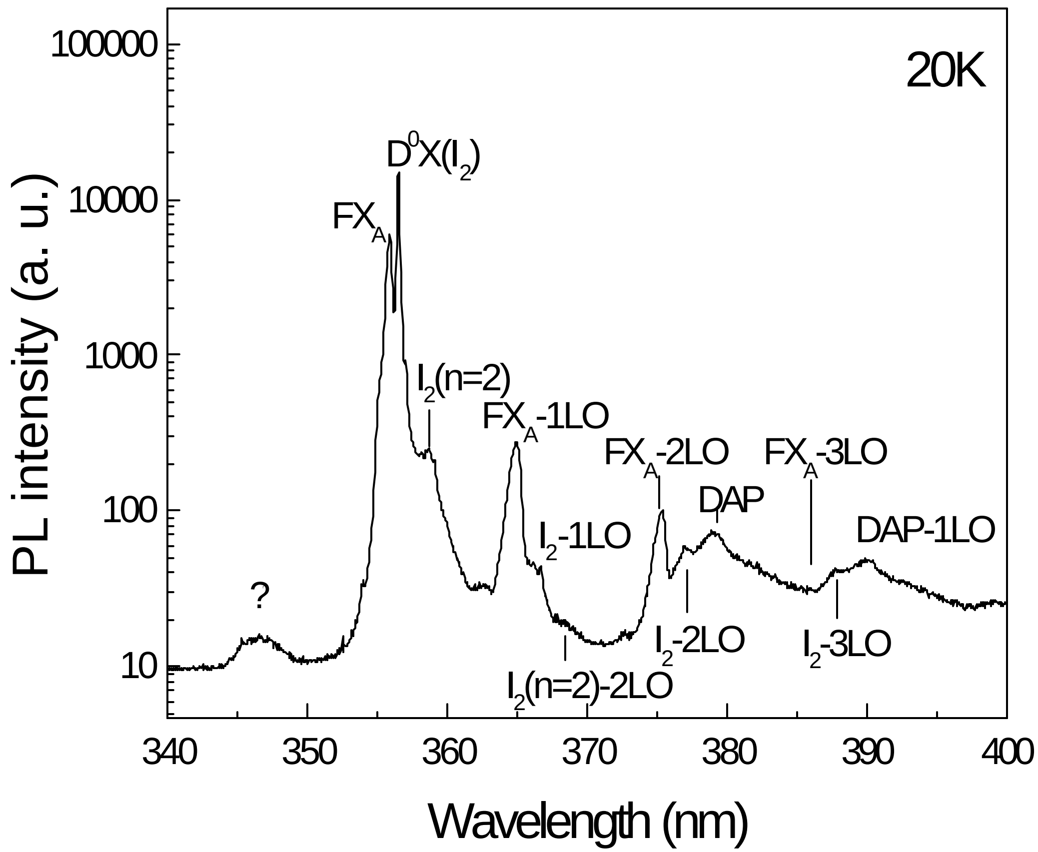
GaN Properties With and Without Buffer Layer

Comparable optical and structural properties for GaN growth with ZnO buffer layer and directly on sapphire.



- Sample thickness: ~ 30 μm
- FWHM of XRD (0002) ω rocking curve: 350 arcsec.
- CV carrier concentration: $\sim 10^{16}/cm^3$
- Low temperature (20 K) PL spectra: strong optical emission related to bound-donor or free excitons and their phonon replica.

Optimized GaN Growth



- Thickness ~30 μm
- XRD (0002) ω rocking curve: 270 arcsec
- Improved surface morphology (pits and crack-free).
- Intensity of the DAP: significantly reduced.

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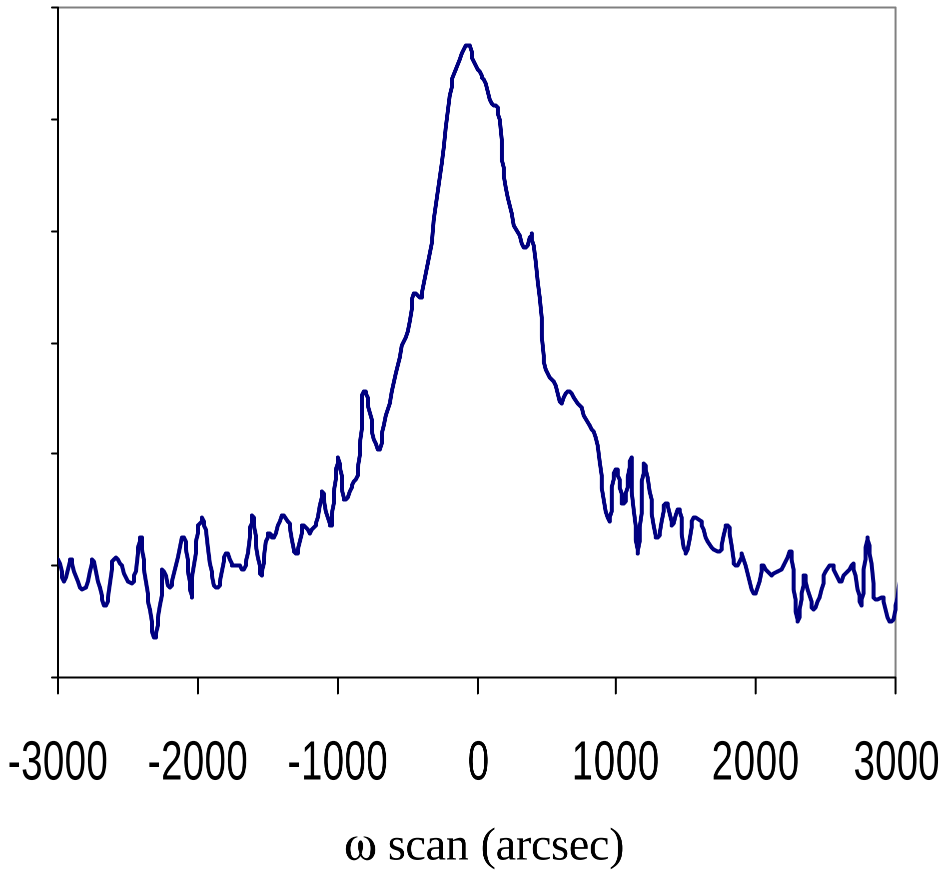
HVPE AlN



XRD (0002) at 18.069°

ω rocking curve: 1050”

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Program Accomplishments to date:

- Developed general models of HVPE growth extendable to AlGaN
- Developed new HVPE reactor system for growth of AlGaN
- Produced low carrier concentration HVPE GaN
- Improved buffer layer and surface treatment techniques
- Extended the growth of ELO to small pattern dimensions with a commensurate improvement in the defect density

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Upcoming tasks

- Demonstrate growth of the full range of AlGaN compositions
- Apply them to improved Schottky devices and determine detailed electronic materials properties relevant for high power.

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